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Original article

Hydrocarbons and monoesters of propolis waxes from Brazil

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Abstract – Waxes of 23 samples of propolis of *Apis mellifera* mostly from Brazil yielded monoesters as main constituents, followed by hydrocarbons. The methyl and acetyl esters of the carboxylic acids and alcohols, respectively, derived from the monoesters, and the hydrocarbons were analysed by gas chromatography/electron impact-mass spectrometry. The hydrocarbons comprise *n*-alkanes and alkenes, the main homologues being $C_{27}H_{56}$, $C_{29}H_{60}$, $C_{31}H_{64}$ and $C_{33}H_{68}$. *iso*-Alkanes in low amounts were found in some samples. The main carboxylic acids are $C_{16:0}$, $C_{18:0}$, $C_{18:1}$. The primary alcohols range from C_{24} to C_{34}, C_{30} being generally the main constituent. A wide variation in the distribution of hydrocarbons, acids and alcohols was found comparing one sample with another. The composition of propolis wax is similar to that of comb wax, which suggests that propolis waxes are probably secreted by the bees, rather than originating from plants. © Inra/DIB/AGIB/Elsevier, Paris

***Apis mellifera* / propolis / waxes / hydrocarbon / monoester**

1. INTRODUCTION

Propolis is a resinous substance used by bees as a sealer for their hives and as a means of preventing decomposition of animals killed after invading the colony [8]. Many biological and pharmacological properties are ascribed to propolis [12]. A wide range of substances have been found in samples of propolis: pollen, waxes, phenolics, resins, aromatic and ethereal oils, and other organic substances. The phenolic content of pro-

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polis, characterized chiefly by flavonoid aglycones, phenolic acids and their esters [3], has deserved much more attention by the investigators than the waxy content.

The term 'waxes' commonly refers to mixtures of long-chain apolar compounds found on the surface of plants and animals [10]. Beeswax refers to the wax present in hives of bees of the genus *Apis*, mainly the European bee *A. mellifera* L. It consists chiefly of mixtures of hydrocarbons, complex esters and free acids [19].

Samples of propolis contain a whitish material which can be obtained by hot alcoholic treatment, followed by cooling the extract. In comparison to beeswax, much less is known about the composition of propolis waxes. Substances commonly found in insect wax, such as alkanes, alkenes, alkadienes, monoesters, diesters, aromatic esters, ketones and fatty acids [14], were found in propolis by Seifert and Haslinger [16, 17]. Other researchers [4, 8, 9] have found in propolis similar mixtures of compounds.

The bees presently found in Brazil are genetically quite distinct from the bees found, for example, in Europe and North America. In Brazil there has been an extensive hybridization between the European bees *A. mellifera mellifera* and *A. mellifera ligustica* with the African bee *A. mellifera scutellatai*, after the introduction of the latter in the 1950s. Contemporarily, *A. mellifera* bees in Brazil are said to be Africanized. Propolis from Brazil and products derived therefrom have been shown to present antibacterial properties [13, 20].

The composition of propolis waxes from Brazilian sources is practically unknown. Bankova et al. [2] reported long-chain alkanes in two out of four samples of propolis from Brazil. The aim of the present work is to separate, quantify and determine the composition of the main constituent classes of propolis waxes from different parts of Brazil and verify to what extent they differ from one sample to another.

2. MATERIALS AND METHODS

2.1. Samples

Samples of propolis were collected from hives grown in different parts of Brazil, ranging from the Northeast (one sample from the state of Ceará) to the South (states of Paraná and Rio Grande do Sul). One sample was collected in Uruguay. Most samples were collected in the states of São Paulo (Southeast Brazil) and Rio Grande do Sul (*table I*).

2.2. Extraction of the waxes

Amounts of propolis ranging from 30 to 80 g were powdered and treated with ethanol in Soxhlet extractors for 6 h. By cooling the extracts, a whitish material separated, which was washed with cooled ethanol. The waxes were dried in the air and in a dessicator until a constant weight was achieved.

2.3. Separation of the constituent fractions

The samples of waxes (1–3 g) were dissolved in a small volume of chloroform and incorporated in silicagel (Merck, 20–70 Mesh). After evaporation of the solvent the mixture was deposited on top of a column (4.5 cm × 40 cm) of silicagel (Merck, 20–70 Mesh). The wax constituents were eluted with the following solvents: *n*-hexane, *n*-hexane:chloroform (2:1, 1:1, 1:2) and chloroform. The eluted fractions were purified by preparative TLC on laboratory prepared plates of silicagel G (Merck, Typ 60) impregnated with sodium fluoresceine. The silicagel slurry was prepared using a solution of sodium fluoresceine 0.02 %. A mixture of *n*-hexane:chloroform (73:27) was used as solvent. The following reference compounds were used to aid in the chromatographic characterization of the wax fractions: octacosane (*n*-alkanes), triacontylhexadecanoate (monoesters), 16-hentriacontanone (ketones), tritriacontane-16,18-dione (β-diketones), 16-hydroxy-hentriacontane (secondary alcohols), triacontanol (primary alcohols) and stearic acid (free carboxylic acids). The chromatograms were visualized under long wave UV [15]. The hydrocarbons and esters were eluted from the adsorbent with chloroform. Functional characterization of the constituent fractions was achieved by IR spectrometry with a Perkin-Elmer equipment, model FTIR.

Table I. Samples of propolis and respective contents (%, w/w) of wax, wax hydrocarbons and monoesters.

Sample, origin*	Wax	Hydrocarbons	Monoesters
1. Pacajus, Ceará	7.0	37.5	58.0
2. Estiva, Minas Gerais	9.2	10.7	70.9
3. Ribeirão Preto, São Paulo	3.1	23.3	66.7
4. Araraquara, São Paulo	4.9	22.5	75.0
5. Rio Claro, São Paulo	9.4	25.4	72.9
6. Limeira, São Paulo	6.0	1.2	88.2
7. Jarinu, São Paulo	12.0	24.5	71.0
8. Mairiporã, São Paulo	5.5	12.7	86.7
9. Mogi das Cruzes, São Paulo	7.4	14.5	77.4
10. Prudentópolis, Paraná	6.0	33.5	61.2
11. Prudentópolis, Paraná	12.4	11.5	74.5
12. Ponta Grossa, Paraná	6.1	9.3	78.9
13. Marechal Rondon, Paraná	10.0	5.8	87.6
14. Salto de Itararé, Paraná	2.3	24.7	75.3
15. Curitiba, Paraná	14.0	8.0	87.1
16. Taquara, Rio Grande do Sul	4.1	2.7	81.7
17. Taquara, Rio Grande do Sul	12.0	11.0	87.3
18. Arroio Ratos, Rio Grande do Sul	11.1	16.5	72.4
19. Bocaiuva, Rio Grande do Sul	11.5	10.5	77.1
20. Alegrete, Rio Grande do Sul	4.1	18.2	80.9
21. Cambará do Sul, Rio Grande do Sul	7.8	8.4	88.5
22. Cambará do Sul, Rio Grande do Sul	9.2	20.0	79.7
23. Porto Alegre, Rio Grande do Sul	16.4	14.7	81.3
24. Uruguay	9.6	12.2	83.3

* Except for sample 24, names of Brazilian municipalities and respective states are given.

2.4. Hydrolysis of the esters and derivatization of the resulting acids and alcohols

The esters were treated with 15 mL of 15 % methanolic KOH under reflux for 6 h. The solution was cooled to room temperature and neutralized with 10 % HCl and extracted three times with 20 mL chloroform. The chloroform extract was concentrated and chromatographed on preparative TLC plates, according to the procedure described above, using chloroform as solvent. The alcohols were eluted from the adsorbent with chloroform and the acids with chloroform:acetic acid (3:1).

The alcohols were acetylated by treatment with 15 mL of acetic anhydride under reflux for 6 h. After cooling to room temperature, 20 mL of water was added and the mixture was kept for 24 h for hydrolysis of the excess acetic anhydride. The mixture was neutralized with a saturated solution of sodium bicarbonate and extracted three times with chloroform. After treatment with anhydrous sodium sulphate, the chloroform extract was evaporated under reduced pressure.

The acids were methylated with an ethereal solution of freshly prepared diazomethane.

2.5. Gas chromatography/mass spectrometry

The hydrocarbons and the derivatized acids and alcohols were dissolved in diethyl ether. 1 µL of the ethereal solutions was injected on an HP 5890 series II GC, interfaced with an HP 5989B

ChemStation System mass spectrometer (Hewllett-Packard), operating with the EI mode at 70 eV. An HP Ultra-1 capillary column of fused silica (25 m × 0.3 mm) was used, oven temperatures ranging from 100 to 230 °C at 3 °C.min^{-1} and an isothermal period of 25 min. Injector and detector temperature was 250 °C. Reference compounds of hydrocarbons (Polyscience), methyl esters of acids and acetyl esters of alcohols (Sigma) were used to aid in the identification of the constituent homologues, as well as comparison of the mass spectra obtained with data of the library Wiley275. The amount of each component was determined by integration of the areas of the corresponding peaks and comparison with the areas corresponding to known amounts of standards.

3. RESULTS AND DISCUSSION

The contents of wax and its constituent hydrocarbons and monoesters in the samples of propolis analysed are shown in *table I*. The amounts of wax range from 2 to 16 %, figures that are relatively small as compared to some of the contents reported by [6], which come close to 30 % for samples of propolis from China.

Monoesters (58–88.5 %) were the major constituents of the propolis waxes studied, followed by hydrocarbons (1.2–37.5 %) (*table I*). A difference between beeswax and plant waxes seems to lie in the contents of primary alcohols, which are often major constituents of the latter [1, 5], and are minor components or absent in the former [14, 19]. In contrast, free fatty acids are rare in plant waxes and relatively abundant in beeswax. In addition to hydrocarbons and monoesters, the wax from combs of *Apis mellifera* has been found to contain diesters, triesters and other minor fractions [14, 19]. In the present investigation, we found no fractions corresponding to diesters and triesters in propolis wax. In TLC, they are found close to the monoesters, with Rf decreasing according to the number of constituent residues [19]. Lambremont and Wikle (apud Hepburn [11]) also did not find diesters in virgin wax of *Apis mellifera.*

The main constituents of the hydrocarbon fractions are *n*-alkanes (*table II*). Some samples presented low amounts of *iso*-alkanes (2-methylalkanes), with mass spectra presenting peaks at M-43 (loss of isopropyl) and M-15 (loss of methyl). IR spectroscopy of the hydrocarbons showed weak bands indicative of unsaturated hydrocarbons (966.7 and 1627.8 cm^{-1}).

Table II presents the distribution of hydrocarbons of the samples analysed. *n*-Alkanes with odd numbers of carbon atoms predominate, *n*-C_{27} appearing in most samples as the main homologue. In some cases, *n*-C_{31} appears as the main hydrocarbon (samples 2, 6, 8, 12, 13, 16, 17 and 24, *table II*). Some of these samples, for example 16 and 17, came from the same locality, others are from close localities, for example 12 and 13. It must be observed, however, that other samples collected from close sites presented different main hydrocarbons, such as samples 6 and 7 (*table II*). The samples differ also in the presence or relative concentration of branched and unsaturated hydrocarbons. Samples 6, 15, 16, 21 and 24 presented exclusively *n*-alkanes in the hydrocarbon fraction; samples 12 and 17 presented additionally *iso*-alkanes, and samples 3, 13, 20 and 23 presented alkenes. Samples 1, 2, 4, 5, 7, 8, 9, 10, 11, 14, 18, 19 and 22 presented the most complex hydrocarbon fraction, mixing *n*-alkanes, *iso*-alkanes and alkenes (*table II*). In general, *iso*-alkanes and alkenes were absent or appeared as minor components in the propolis waxes investigated. However, samples 18 and 19 (from close localities of the state of Rio Grande do Sul) were unusual for the absence of *n*-C_{29}, which is substituted by *iso*- C_{29}. Samples 7, 9 and 14 were unusual by the relatively high percentages of alkene C_{33} (*table II*). Downing et al. [7] found 16 % of hydrocarbons in a sample of beeswax, comprising homologues in the range C_{25}–C_{33}. Streibl et al. [18] showed that about 31 % of the hydrocarbons of a sample of beeswax consisted of *cis*-olefins, mainly with 31 and 33 carbon atoms, whereas the *n*-alkanes

Table II. Percentual distribution of homologues in the hydrocarbon fraction of samples of propolis waxes. Unless stated, numbers of carbon atoms correspond to normal chains; *iso* = 2-methyl isomers; colon followed by digit 1 indicates one unsaturation. Digits on sample column correspond to samples listed in *table I*.

Sample	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	*iso*-C_{27}	C_{28}	C_{29}	*iso*-C_{29}	C_{30}	C_{31}	$C_{31:1}$	*iso*-C_{31}	C_{32}	C_{33}	$C_{33:1}$	$C_{35:1}$
1	1	1	7	1	23	1	38		1	10	1	1	7	1	1		1	4	1
2			3	1	8	1	24	1	1	14	2	1	26	1	1		5	8	3
3			4	1	16	2	38			16			16	1			2	4	
4			2	1	8	1	27	1	1	16	4	1	25	1	5		2	4	1
5			1	1	9	1	31	1	1	18	3	1	22	1	3		3	3	1
6							15			29			46				10		
7			1		9	1	27		1	16	2	1	23	2	2		4	9	2
8			2		7	1	25	1	1	17	5	1	27	1	3		3	5	1
9			2	1	7	1	26		2	13	2	1	25	2	1		5	10	2
10	1	1	3	1	21	1	38		1	14	1	1	11		1		1	4	
11			1		8	1	29		3	22	2	1	25	1	1		4	2	
12					2	1	22		1	25	1	2	38		2		6		
13			1		6	1	29		1	20		1	33				5	2	1
14			1		5	1	26		1	18	4	1	24	1	4		3	10	1
15					6	2	34		3	22		1	28				4		
16							6			22			58				14		
17					2		28		1	25	1	1	37				5		
18			1		3	1	34		1		23	1	23				6	6	1
19			1		10	1	38		1		19	1	24				1	4	
20					6	1	32		1	20		1	30			1	6	1	1
21					6	1	37		1	22		1	28				4		
22			1		9	1	34		1	19	1	1	26	1			3	2	1
23			1		7	1	35		1	19		1	28				4	2	1
24							13			23		2	54				8		

varied within the range C_{25}–C_{29}.Very small amounts of branched chain hydrocarbons and *trans*-olefins were also identified. The data so far available indicates that, although highly variable, the hydrocarbon composition of comb and propolis wax seem to be similar, at least with regard to the range of carbon chains and to constituent functions.

Our finding of *n*-C_{27} as the main hydrocarbon of propolis waxes is in agreement with Tulloch's results [19], which established the same alkane as the main hydrocarbon of comb waxes of *A. mellifera mellifera* and *A. mellifera adansonii*. The predominance of *n*-hydrocarbons with odd numbers of carbon atoms is a common feature of waxes of plants and animals, because they are biosynthesized by decarboxylation of fatty acids, most of them possessing even numbers of carbon atoms. *iso*-Alkanes are biosynthesized by decarboxylation of fatty acids formed by the addition of C_2 units (via malonyl-CoA) to a L-valine residue, giving rise to hydrocarbons with odd numbers of carbon atoms, or to a L-leucine residue, originating even numbered hydrocarbons [14].

Alkenes seem to be minor constituents of propolis waxes. In fact, Marcucci [12] makes no reference of the presence of alkenes as constituents of propolis, although several alkanes are mentioned, among other lipids. The absence or low amounts of unsaturated hydrocarbons in propolis waxes (*table II*) contrast with data reported for comb waxes, which have been shown to present alkenes ($C_{31:1}$ and $C_{33:1}$) in relatively high amounts in the hydrocarbon fraction [16, 17, 19]. Moreover, unsaturated homologues are very common and often predominate in insect epicuticular waxes, often playing important roles in chemical communication [14]. On the other hand, propolis wax resembles comb wax, as both possess low contents of branched alkanes.

The distribution of wax hydrocarbons has been extensively used as taxonomic aids in botany [5] and entomology [14]. The present results, however, suggest that the hydrocarbons of propolis waxes produced in Brazil are too variable to possess taxonomic meaning at the species level. In addition, no relationship can be drawn between hydrocarbon profiles and geographic proximity of the samples of the present investigation.

The esters of the samples of propolis analysed presented exclusively acid moieties with straight carbon chains, most compounds with saturated chains (*table III*). The main homologue was palmitic acid ($C_{16:0}$), with few exceptions (samples 3 and 24, *table III*). Oleic acid ($C_{18:1}$) appeared in general with amounts close to 10 %, except for samples 6 (23 %), 15 (15 %), 16 (16 %) and 24 (from Uruguay, 50 %). The relative proportions of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ varied widely from one sample to another. The alcohol moieties found are exclusively saturated *n*-homologues. For most samples, the main homologue found is C_{30}. C_{24} is the main alcohol homologue for samples 1 and 10 (and is the second most important for 11 other samples) while C_{28} appears as the main homologue for sample 23 (and is the second most important for three other samples) (*table III*). Other homologues which appeared with relatively high amounts were C_{32} (second most important homologue for seven samples) and C_{26} (second most important homologue for three samples) (*table III*). Taking into account the most likely combinations of acids and alcohols to form the esters, a range of ester chains is expected from C_{40} to C_{50}. A predominance of esters C_{40}, C_{46} and C_{48} is expected to occur for most samples. Tulloch [19] found monoesters of comb waxes of *A. mellifera mellifera* and *A. mellifera adansonii* ranging from C_{40} to C_{50}. C_{46} was found to be the main homologue monoester, followed by C_{48} and C_{40}. Our results of the analyses of propolis monoesters of Africanized bees closely match Tulloch's results relative to comb monoesters of European and African bees. As was observed with the distribution of hydrocarbons, the distribution of the carboxylic acids and primary alcohols of proplis monoesters varies widely from one sample

Table III. Percentual distribution of constituent *n*-primary alcohols and *n*-carboxylic acids of monoesters of propolis waxes. Colon followed by digit 1 indicates one unsaturation. Digits on sample column correspond to samples listed in *table I*.

Sample/ fraction	C_{14}	C_{16}	C_{18}	$C_{18:1}$	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30}	C_{32}	C_{34}
Alcohols												
1			1		1	1	38	24	19	14	2	
2							22	16	16	33	13	
3							26	17	18	31	8	
4						2	9	11	17	34	27	
5						1	22	17	19	35	6	
6					4		18	20	18	33	7	
7							23	16	16	30	15	
8						1	10	10	17	46	16	
9						2	21	15	15	31	16	
10					1	1	34	19	25	17	3	
11						1	21	18	17	29	13	1
12							28	18	18	30	6	
13					1	1	18	14	15	29	19	3
14						1	5	8	12	41	30	3
15						1	12	11	14	38	24	
16					2	10	16	10	14	27	20	1
17					1	2	9	10	14	35	26	3
18					2	4	17	11	13	30	21	2
19							23	18	19	31	9	
20							22	16	16	30	16	
21							20	14	18	34	14	
22						2	28	19	16	26	9	
23					2	21	14	15	30	14	4	
24							17	22	22	34	5	
Acids												
1		72	17	10			1					
2		69	21	7	1	2						
3		41	41	10	4	2	2					
4		70	17	9	2	2						
5		55	34	10	1							
6		44	10	23	1	1	8	12	1			
7		79	11	10								
8		75	11	11	1	1	1					
9		79	11	8	1		1					
10		76	12	11			1					
11	1	57	29	12	1							
12		80	12	5	1	1	1					
13		69	21	4	3	1	1	1				
14		85	7	8								
15	1	58	3	15	2	6	7	3	4	1		
16		78	5	16			1					
17		76	14	10								
18	1	45	37	11	3	1	2					
19		75	14	8	1	1	1					
20		64	15	4	8	8	1					
21		65	22	6	3	2	2					
22		65	24	4	3	2	2					
23		90	5	5								
24		34		50			16					

to another. No correlation seems to exist between locality and homologue distribution of constituent acids and alcohols of monoesters. It is true that samples 16 and 17, from Taquara, are very similar relative to the distribution of acids and alcohols (*table III*). Samples 21 and 22, however, both from Cambará do Sul, are quite similar relative to the distribution of acids, but are rather different as to the distribution of alcohols. Samples 10 and 11, both from Prudentópolis, presented rather dissimilar distributions of acids and alcohols (*table III*). The wide variability among the distribution of the homologues of the monoester constituents of the propolis waxes studied make them unreliable taxonomic markers at the species level.

A comparison between the results of the present investigation and data from the literature relative to the composition of comb waxes reveals a general similarity between the latter and propolis waxes, although notable differences are apparent as to the relative proportions of some constituents. This observation suggests that propolis waxes are produced by bees, in a way similar to the comb waxes. The possibility that propolis waxes are derived from plants visited by bees is extremely low due not only to the similarities in composition of comb and propolis wax, but also to the virtual absence of residues of oleic acid in wax esters from plants [5]. The differences between the propolis waxes studied in the present work and the comb waxes reported in earlier literature may be a consequence of genetic differences between races of *A. mellifera* from distinct localities, differences due to hybridization between the African and the European bees or they may reflect differences in the secretory process. Studies of comb wax and propolis wax produced by the same colony will be necessary to establish the degree of similarity between both types of wax and thus help answer these questions.

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Résumé – Hydrocarbures et mono-esters présents dans les cires de propolis du Brésil. Les cires de 23 échantillons de propolis d'*Apis mellifera* provenant de plusieurs localités du Brésil et d'une localité d'Uruguay ont été fractionnées en classes de constituants. Les principaux constituants rencontrés sont des mono-esters puis des hydrocarbures (*tableau I*). Les esters ont été hydrolysés et leurs acides carboxyliques et les alcools primaires ont été convertis en esters de méthyle et en esters d'acétyle respectivement. Les hydrocarbures et les esters de méthyle et d'acétyle ont été analysés par chromatographie en phase gazeuse couplée à la spectrométrie de masse, en utilisant la technique d'impact électronique. Les hydrocarbures présentent un mélange complexe de *n*-alcanes et d'alcènes avec un nombre impair d'atomes de carbone, compris dans l'intervalle C_{23} à C_{35}, tandis que les alcènes et *iso*-alcanes sont présents en quantités moindres. Les principaux hydrocarbures observés sont : $C_{27}H_{56}$, $C_{29}H_{60}$, $C_{31}H_{64}$ et $C_{33}H_{68}$ (*tableau II*). Le principal acide carboxylique dérivé des esters est le $C_{16:0}$, suivi par le $C_{18:0}$ et le $C_{18:1}$. Les alcools primaires dérivés des esters sont plutôt des *n*-homologues saturés, avec un nombre pair d'atomes de carbone, compris dans l'intervalle de C_{24} à C_{34}, le C_{30} étant majoritaire dans la plupart des cas (*tableau III*). On constate une grande variation de la répartition des hydrocarbures, des acides et des alcools d'un échantillon à l'autre. Cette observation suggère que les hydrocarbures et les esters des cires de propolis ne représentent pas un caractère taxonomique fiable au niveau de l'espèce pour les populations

d'*Apis mellifera* du Brésil. La composition similaire entre la cire de propolis et la cire des alvéoles suggère que la cire de propolis est synthétisée par les abeilles et non dérivée des plantes. © Inra/DIB/AGIB/Elsevier, Paris

propolis / cire / hydrocarbure / monoester / chromatographie gazeuse / spectrométrie de masse

Zusammenfassung – Kohlenwasserstoffe und Monoester von brasilianischen Propolis-Wachsen. Die Bestandteile der Wachse von 23 Propolis-Proben von *Apis mellifera* aus mehreren Standorten in Brasilien und einem in Uruguay wurden durch Säulen- und Dünnschichtchromatographie aufgetrennt. Den Hauptbestandteil bildeten Monoester, gefolgt von Kohlenwasserstoffen. Die Ester wurden hydrolysiert und die Karbonsäuren und primären Alkohole wurden in ihre entsprechenden Methyl-, beziehungsweise Acetylester umgewandelt. Die Kohlenwasserstoffe, Methyl- und Acetylester wurden durch Gaschromatographie in Kombination mit Elektronenimpakt-Massenspektrometrie analysiert. Die Kohlenwasserstoffe bestehen hauptsächlich aus einem komplexen Gemisch von n-Alkanen, die eine ungerade Anzahl von Kohlenstoffatomen im Bereich von C_{23}-C_{35} besitzen. Die am häufigsten vorhandenen Kohlenwasserstoffe sind $C_{27}H_{56}$, $C_{29}H_{60}$, $C_{31}H_{64}$ und $C_{33}H_{68}$. Zusätzlich wurden Alkene und Isoalkane in geringeren Mengen gefunden. Die häufigste Karbonsäure der Ester ist $C_{16:0}$ gefolgt von $C_{18:0}$ und $C_{18:1}$. Die primären Alkohole der Ester sind vorwiegend gesättigte n-Homologe mit einer geraden Anzahl an Kohlenstoffatomen im Bereich von C_{24}-C_{34}, mit C_{30} als dem am häufigsten vorkommenden Bestandteil. Die Verteilung der Kohlenwasserstoffe, Säuren und Alkohole variierte sehr stark von Probe zu Probe. Daher können die Kohlenwasserstoffe und Ester von Propolis-Wachsen nicht zuverlässig als taxonomische Merkmale von Populationen von *Apis mellifera* aus Brasilien herangezogen werden. Es wurde eine Ähnlichkeit in der Zusammensetzung der Propolis-Wachse im Vergleich zur Zusammensetzung der Waben-Wachse festgestellt (letzteres basiert auf Literaturangaben), was darauf hinweist, daß Propolis-Wachse von Bienen ausgeschieden werden und höchst wahrscheinlich nicht von Pflanzen stammen. © Inra/DIB/AGIB/Elsevier, Paris

Propolis / Wachse / Monoester / Kohlenwasserstoffe / Gaschromatographie-Massenspektrometrie

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